

Lanthanum uptake from soil and nutrient solution and its effects on plant growth

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Accepted June 11, 2005

PNSS P05/06P

Summary—Zusammenfassung

In view of restrictions in the application of antibiotics in animal production, Lanthanum (La) is intended to be introduced as a new growth promoter for pigs. Because most of the supplied La is subsequently excreted, it will be found in organic fertilizers which are applied to agricultural land. Thus, we examined the effect of lanthanum on the growth and La contents of plants in nutrient solution and in soils as well as its extractability from different soils. In nutrient solutions with concentrations of available La of up to $20 \mu\text{mol L}^{-1}$, shoot growth of bush bean was markedly reduced by up to 60% of the control at $20 \mu\text{M}$ La. By contrast, growth was not affected in maize. Lanthanum was mainly accumulated in the roots, but maize shoot contained considerable amounts of La as well. In contrast to nutrient solution, shoot growth of bush bean and spinach in soils supplemented with La up to $360 \mu\text{mol kg}^{-1}$ (50 mg kg^{-1}) was not decreased. In contrast to spinach, bush bean shoots showed an increased La content at the highest La level. Extractability of La with 0.1 mol L^{-1} acetic acid from 12 different soils previously spiked with La was related mainly to soil pH, CEC, and C_{org} . We therefore conclude that except of strongly acidic conditions, the application of La-containing organic fertilizers does not represent a risk for plant growth for the next over 100 years, provided that the recommended doses of feed supplementation is not increased.

Key words: bush bean / lanthanum / La bioavailability / La solubility / maize / rare-earth elements / spinach / soil properties

1 Introduction

Rare-earth elements (REEs) represent a group of 17 transition metals. They comprise scandium, yttrium, and further 15 elements called lanthanides, ranging from the more abundant lanthanum (La) and cerium (Ce) to the less frequent lutetium (Lu). Rare-earth elements are characterized by similar chemical and physical properties (e.g., their ionic radius). With few exceptions, their valence state is +3.

In China, the use of mixtures of REEs in agriculture is widespread and aims at increasing growth of plants and animals. Commercially available mixtures are prepared from mineral ores and consist of all REEs with a predominant proportion of La and Ce (Brown et al., 1990; Xu et al., 2002). Results of positive effects of these additives on crop production are almost exclusively reported in the Chinese literature. Yield in-

Aufnahme von Lanthan aus Boden und Nährlösung und Auswirkungen auf das Pflanzenwachstum

Angesichts der Einschränkungen im Einsatz von Antibiotika in der Tierfütterung besteht die Absicht, Lanthan (La) als neuen Leistungsförderer in der Schweinemast einzusetzen. Da der überwiegende Teil des verfütterten La vom Tier ausgeschieden wird, gelangt La über den Einsatz von Wirtschaftsdüngern in das Agrarökosystem. Daher wurde der Einfluss von La auf das Wachstum und die La-Gehalte von Pflanzen sowie die La-Extrahierbarkeit aus verschiedenen Böden untersucht. In Nährlösung wurde das Sprosswachstum von Buschbohne durch ein verfügbares La-Angebot von $20 \mu\text{mol L}^{-1}$ im Vergleich zur Kontrolle um etwa 60% reduziert. Das Wachstum von Mais wurde dagegen nicht beeinflusst. Lanthan wurde vor allem in den Wurzeln akkumuliert, jedoch wies auch der Spross von Mais erhöhte La-Gehalte auf. Im Gegensatz zur Nährlösung verringerten La-Zusätze von bis zu $360 \mu\text{mol kg}^{-1}$ (50 mg kg^{-1}) zum Boden das Wachstum von Buschbohne und Spinat nicht. Im Unterschied zu Spinat war bei der höchsten La-Zugabe der La-Gehalt im Spross von Buschbohne erhöht. Die Extrahierbarkeit von La mit 0.1 mol L^{-1} Essigsäure aus 12 verschiedenen, zuvor mit La versetzten Böden wurde hauptsächlich durch den pH-Wert des Bodens, die KAK und den Gehalt an organischer Substanz bestimmt. Es lässt sich daher schlussfolgern, dass, außer unter sehr sauren Bedingungen, eine Schädigung für das Pflanzenwachstum durch die Ausbringung La-haltiger Wirtschaftsdünger über einen Zeitraum von mehr als 100 Jahren kaum zu erwarten ist, vorausgesetzt, die bisher empfohlene La-Dosierung in der Fütterung wird nicht erhöht.

creases were observed for numerous crop species under various cultivation and application systems (e.g., application to roots, shoots, or seed) and both in nutrient solution and under soil conditions. The enhancement of biomass production is reported to range between 8% and 50%, with an average yield increase of 8%–15% (Brown et al., 1990; Hu et al., 2004). In addition, REEs are claimed to improve the nutritional quality and to be effective predominantly under stress conditions.

However, results about the influence of REEs on plant development are contradictory. Beneficial effects may be restricted to certain growth stages. In *Arabidopsis thaliana*, for example, only root growth, floral initiation, and reproductive shoot development were stimulated by La and Ce in concentrations of about 0.5 to $10 \mu\text{mol L}^{-1}$ (He and Loh, 2000). Vegetative growth was not affected at these concentrations and inhibited when higher. Diatloff et al. (1995 a, b) showed that very low La and Ce concentrations in nutrient solution (up to about $1.4 \mu\text{mol L}^{-1}$) did not affect the shoot growth of maize, but

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significantly decreased the shoot dry weight of mungbean. By contrast, some beneficial effects on root growth of maize were observed at these concentrations, while concentrations above $2 \mu\text{mol L}^{-1}$ caused appreciable reductions in root elongation (Diatloff et al., 1995c).

It was concluded, that the impact of REEs on plant development depends on the growth medium. Lanthanum in concentrations from 3.5 to $72 \mu\text{mol L}^{-1}$ increased dry-matter production of barley, canola, and ryegrass by up to 90%, 38%, and 78%, respectively, when the plants were cultivated under greenhouse conditions in perlite with Hoagland's nutrient solution (Pevevill et al., 1997). When plants were grown in soil, yields were unaffected, except in a loamy sand, where the yield was increased under drought conditions. Also, in the field, virtually no effect of La on biomass production was observed.

These observations could be explained by the fact that the behavior of REEs in soil is related to properties of the soil. Low pH values (Diatloff et al., 1996; Cao et al., 2001; Yufeng et al., 2001), but also lower cation-exchange capacity (CEC), organic-matter content (Jones 1997; Shan et al., 2002), and redox potential (Cao et al., 2001) all increase the solubility of REEs in soils. The addition of organic acids was found to decrease the adsorption of REEs to soil (Shan et al., 2002). Furthermore, the presence of REE- PO_4 (Johannesson et al., 1995; Diatloff et al., 1996) and metal-(hydr)oxides (Janssen and Verweij, 2003) are thought to play a role in the mobility of REEs. Therefore, it was concluded that, compared to their high availability in nutrient solution, the risk of toxic effects of REEs on plant growth is lower when REEs are added to soil. This is in line with the observation that humic and fulvic acids, which are commonly present in soil solution, may overcome the rhizotoxicity of La by complex formation (Diatloff et al., 1998).

Soil properties may also affect the uptake of REEs by plants. It is generally accepted that the total REE content in soil is a poor indicator for the prediction of plant uptake. For the determination of plant availability in unamended (Li et al., 1998) and REE-treated soils (Zhang and Shan, 2001), a sequential extraction procedure based on a European Community Bureau of Reference (BCR) Standard has been used. In both categories of soil, the REE contents of rice, corn, and wheat were significantly correlated with the fraction of water-soluble, exchangeable, and carbonate-bound REE species that are extracted by 0.1 mol L^{-1} acetic acid. However, these correlations varied according to the different plant organs like roots, leaves, or grains. In addition, the uptake and contents of REEs in plants differ considerably between plant species, even under natural conditions without supplementation (Ichihashi et al., 1992; Wytenbach et al., 1998).

As the use of antibiotics in animal production is largely restricted, the application of REEs as alternative growth promoters has been initiated in Germany (He et al., 2001; Schuller et al., 2002). Fodder-supplementation with La and Ce increased daily weight gain by up to 19% and improved food conversion of up to 11% for pigs. The accumulation of La and Ce in animal organs was very low (He et al., 2001). Conse-

quently, most of the added La and Ce will be found in the excrements, which are returned as organic fertilizer to agricultural land. It is therefore essential to assess the potential risks of the regular addition of REEs to soil ecosystems. One factor for this risk assessment is evaluating the release of REEs from the solid phase to the soil solution and other easily soluble fractions, which are closely related to their bioavailability. Although most of the accumulated REEs are retained by the soil, certain conditions like acidification by acid precipitation may mobilize them, so that they may be leached into the groundwater (Yufeng et al., 2001). Higher concentrations of La may cause significant damage to the ecosystem (Barry and Meehan, 2000).

In view of the intended application of La and Ce for animal production in Germany, investigations into the effects of these elements on the plant-soil ecosystem are required. The aim of this study was to evaluate (1) the effect of available La on the growth of several plant species, (2) the influence of La on plants grown in soil, and (3) the possible role of different soil properties on the solubility and potential plant availability of La in German soils so far not treated with La. From these data, the potential risk of an eventual accumulation of La and its possible transfer into plants was assessed.

2 Material and methods

2.1 Nutrient solution experiment

Seeds of bush bean (*Phaseolus vulgaris* L. var. *nanus* "Daisy") and of maize (*Zea mays* L. var. *saccharata* "Starlite F1 hybrids") were sown into a substrate of expanded clay granules (3–6 mm) and irrigated with a mixture of 1 mmol L^{-1} $\text{Ca}(\text{NO}_3)_2$ and 1 mmol L^{-1} K_2SO_4 . After 9 d, seedlings were transplanted to 65 L plastic containers (10 plants per pot) and fixed into a 2 cm Styrofoam disc that was used as lid.

The nutrient solution was composed of 2 mmol L^{-1} N as NO_3^- and 0.5 mmol L^{-1} N as NH_4^+ , 1 mmol L^{-1} Ca as $\text{Ca}(\text{Cl})_2$, 0.05 mmol L^{-1} P as KH_2PO_4 , 2 mmol L^{-1} K as KH_2PO_4 and K_2SO_4 , 0.75 mmol L^{-1} Mg as MgSO_4 , 0.05 mmol L^{-1} Na as NaCl, and $60 \mu\text{mol L}^{-1}$ Fe as Fe-EDDHA, $11 \mu\text{mol L}^{-1}$ B as H_3BO_3 , $5 \mu\text{mol L}^{-1}$ Mn as MnCl_2 , $0.5 \mu\text{mol L}^{-1}$ Zn as ZnSO_4 , $0.2 \mu\text{mol L}^{-1}$ Cu as CuSO_4 , and $0.01 \mu\text{mol L}^{-1}$ Mo as Na_2MoO_4 . After a phase of adaptation of 7 (bush bean) or 13 (maize) d, lanthanum was applied as LaCl_3 in concentrations of 0, 1, 2, 10, or $20 \mu\text{mol L}^{-1}$, and plants were cultivated for a further 21 or 29 d, respectively.

To maintain the solubility of La, solution pH was adjusted to 4.2 with HCl, and, in case of maize, by additionally adapting the $\text{NH}_4^+ : \text{NO}_3^-$ ratio during growth. Lanthanum and macronutrient concentrations, and pH values were measured and adjusted every two days as required. Nutrient solutions were exchanged once a week. Growth conditions were: day/night period 14/10 h; PAR $450 \mu\text{mol m}^{-2} \text{ s}^{-1}$; temperature, $24^\circ\text{C}/18^\circ\text{C}$ (day/night); and relative humidity 60%/75% (day/night).

At harvest, shoots and roots were separated. Roots were thoroughly washed with demineralized water and carefully

dried with soft tissue. After biomass determination, ground plant material was digested in closed pressurized vessels with HNO_3 and H_2O_2 in a microwave oven, and La was analyzed by ICP-OES, model Liberty RL Sequential, (Varian Australia, Pty, Ltd., Mulgrave, Australia) at 333.749 nm.

2.2 Pot experiments

Seeds of bush beans (*Phaseolus vulgaris* L. var. *nanus* "Daisy") were germinated in expanded clay as mentioned above. After 10 d, seedlings were transplanted to pots with 0.4 kg of a sandy soil, where they were cultivated for 34 d (1 plant per pot). Soil characteristics were as follows: $\text{pH}_{\text{CaCl}_2}$ 5.1; P content 13 mg kg^{-1} (CAL extract; Schüller, 1969); N_t 0.2 g kg^{-1} ; C_{org} 0.5 g kg^{-1} ; CEC 43.8 $\text{mmol}_c \text{kg}^{-1}$; and soil texture 88% sand, 9% silt, and 3% clay.

Lanthanum was added as LaCl_3 solution that was thoroughly mixed into the soil to obtain contents of 0, 0.5, 1.0, 2.0, and 10 $\text{mg La (kg soil)}^{-1}$, corresponding to 0, 3.6, 7.2, 14.4, and 71.9 $\mu\text{mol (kg soil)}^{-1}$. The resulting concentrations of the soil saturation extracts (100 g soil dry matter stirred with bidistilled water until reaching the flow limit (25 mL) in two dosages each equilibrated for 24 h at 5°C) remained below the detection limit (0.07 $\mu\text{mol L}^{-1}$).

For plant growth, soil water content was maintained at 210 g kg^{-1} (70% of the maximum water-holding capacity). Bush beans were fertilized with 200 mg N (NH_4NO_3), 200 mg K (K_2SO_4), 50 mg P ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), and 20 mg Mg (MgSO_4) per plant. Conditions in the growth chamber were as mentioned above (see 2.1).

Spinach (*Spinacea oleracea* L. "Matador") was sown into a loamy sand and cultivated (5 plants in a 5 L pot) under greenhouse conditions from November 3, 2003 for 48 d. Soil char-

acteristics were as follows: pH 5.6; P content 60 mg kg^{-1} (CAL extract; Schüller, 1969); K content 123 mg kg^{-1} (CAL extract); total N content 1.5 mg kg^{-1} ; organic carbon 12.3 mg kg^{-1} ; CEC 68.3 $\text{mmol}_c \text{kg}^{-1}$, and soil texture 65% sand, 24% silt, and 11% clay.

Lanthanum was added to the soil as LaCl_3 to obtain contents of 0, 0.5, 2.5, 5, 10, and 50 $\text{mg La (kg soil)}^{-1}$, corresponding to 0, 3.6, 18, 36, 72, and 360 $\mu\text{mol (kg soil)}^{-1}$. The resulting concentrations of the soil saturation extracts (100 g soil dry matter with 31 mL bidistilled water, see above) were below the detection limit with the exceptions of 72 $\mu\text{mol La (kg soil)}^{-1}$ with a concentration of 0.07 $\mu\text{mol La L}^{-1}$ and of 360 $\mu\text{mol La kg}^{-1}$ with 0.36 $\mu\text{mol La (L soil extract)}^{-1}$.

For plant growth, the soil water content was adjusted regularly and kept at a soil matric potential of -15 kPa (soil water content of 145 g kg^{-1}). The supply of mineral nitrogen for spinach from soil and NH_4NO_3 fertilizer was 360 mg N per pot. Additional light was supplied for 14 h a day using Philipps SON-T AGRO 400 lamps. The temperature in the greenhouse was 20°C/16°C (day/night). After harvest, the La content of bush bean and spinach was analyzed as specified above (see 2.1). For both soils, La was extracted from unplanted parallels with 0.1 mol L^{-1} acetic acid (see below 2.3).

2.3 Lanthanum extraction experiments

Twelve soils, covering a wide range of different properties, were spiked with 10 (72 μmol) or 100 mg (720 μmol) La (kg dry soil)^{-1} (Tab. 1). Lanthanum was added as solution to 200 g soil in an amount sufficient to result in a soil-specific water content of 160 to 200 g kg^{-1} . Soils were homogenized by sieving and equilibrated for 2 weeks at 20°C.

Table 1: Selected properties of 12 soils from southern Germany.

Tabelle 1: Ausgewählte Eigenschaften von 12 Böden aus Süddeutschland.

Soil Number	A horizon (FAO, 1998)	Soil type (FAO, 1998)	$\text{pH}_{\text{CaCl}_2}$	P content ^(a)	Organic carbon ^(b)	Total nitrogen ^(b)	CEC _{eff} ^(c)	Sand ^(d)	Clay ^(d)	Silt ^(d)	Acetic acid-extractable La		
											native	spiked with 72	720
				mg kg^{-1}	g kg^{-1}		$\text{mmol}_c \text{kg}^{-1}$	%			$\mu\text{mol kg}^{-1}$		
1	ochric	Arenosol	4.8	22.8	5.5	0.8	27	84	6	10	<0.07	1.37	166.91
2	mollic	Cambisol	5.0	36.6	13.3	1.6	107	55	17	28	0.36	0.86	14.68
3	mollic	Cambisol	5.1	7.2	31.8	3.7	113	27	25	48	<0.07	<0.07	20.07
4	mollic	Cambisol	4.6	7.0	10.2	1.3	86	11	23	66	<0.07	<0.07	17.41
5	mollic	Cambisol	5.8	6.5	11.1	1.3	114	13	22	65	<0.07	<0.07	16.04
6	mollic	Cambisol	6.4	7.0	11.1	1.4	130	11	21	68	<0.07	<0.07	13.24
7	mollic	Cambisol	3.9	30.7	8.8	1.1	79	12	24	64	2.37	7.34	68.13
8	mollic	Cambisol	5.3	27.9	9.9	1.1	109	13	24	63	<0.07	1.08	25.61
9	mollic	Cambisol	6.0	39.1	9.3	1.1	145	13	26	61	<0.07	0.07	6.83
10	umbric	Cambisol	3.7	1.2	11.0	0.9	85	14	22	64	<0.07	10.58	127.48
11	mollic	Cambisol	6.2	61.4	11.9	1.5	155	22	20	58	0.22	1.51	24.32
12	mollic	Gleysol	7.3	87.0	40.2	4.6	421	28	43	29	<0.07	<0.07	0.07

(a) extraction with CAL (Schüller, 1969)

(b) determined with elemental analyzer (vario el, elemental, Hanau, Germany)

(c) determined at actual soil pH

(d) determined by sieving and sedimentation analysis

Water-soluble, exchangeable, and carbonate-bound La in the soil was determined according to Zhang and Shan (2001): 1 g soil (based on dry matter) was shaken with 40 ml 0.1 mol L⁻¹ acetic acid for 16 h at 20°C. Samples were centrifuged (3000 rpm for 7 min), and supernatants were filtered (Schleicher and Schuell 589/2½). Lanthanum was determined by ICP-OES at 379.478 nm.

2.4 Statistical analysis

SPSS 12.0 (SPSS, Inc.) was used for all statistical evaluations. The results of the nutrient solution and the pot experiments were subjected to a one-way analysis of variance with the significance of the means being tested with a Tukey test at $p \leq 0.05$. For the results of the soil experiment, Pearson's correlation coefficients were calculated. Data showing a non-normal distribution were reciprocally ($1/x$) or \ln transformed.

3 Results

3.1 Effect of La in nutrient solution

When bush bean and maize were cultivated in nutrient solution, each plant species responded differently to increasing La concentrations (Fig. 1). The shoot growth of maize and the root dry matter of both species were not affected by concentrations of up to 20 $\mu\text{mol La L}^{-1}$. By contrast, the root elongation of bush bean was severely reduced by about 20% at 1 $\mu\text{mol La L}^{-1}$ and about 90% at 20 $\mu\text{mol La L}^{-1}$ under the same conditions (data not shown). The shoot-biomass production of bush bean decreased continuously with increasing

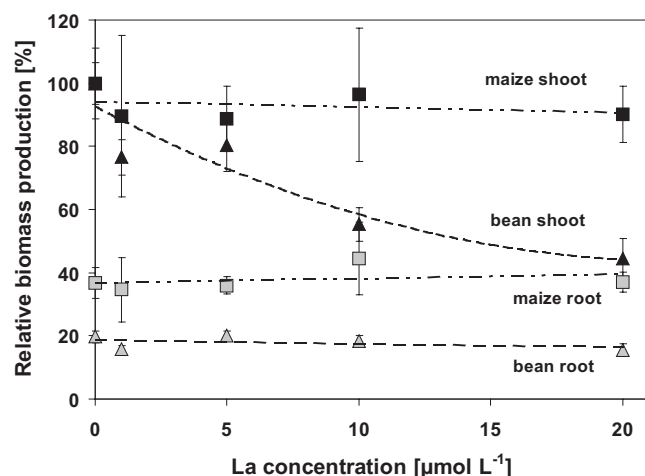


Figure 1: Effect of La concentration on shoot- and root-biomass production (dry weight) of hydroponically grown bush bean and maize. Values are expressed relative to the shoot biomass without added La. Bush bean: 100% corresponds to a shoot dry matter of 5.7 g plant⁻¹; maize: 100% corresponds to a shoot dry matter of 15.1 g plant⁻¹; error bars represent standard deviations.

Abbildung 1: Wirkung von La auf die Bildung der Spross- und Wurzelbiomasse (relativ) von Buschbohne und Mais in Nährlösung. Die Kontrolle ohne La entspricht 100% und einer Sprossstrockenmasse für Buschbohne von 5,7 g Pflanze⁻¹ und für Mais von 15,1 g Pflanze⁻¹; Fehlerbalken geben die Standardabweichung an.

La levels and reached only about 40% of the control at the highest La concentration. No positive influence on growth could be observed at any of the tested La concentrations for any of these plant species.

The effect of the La supply in nutrient solution on the La content in plant organs differed for the two species (Fig. 2). Increasing La concentrations led to a high accumulation of La in bush bean roots, whereas La content in bean shoots was low and obviously not related to the La concentration of the nutrient solution. Compared to the control, the La content of the maize roots was also markedly enhanced in the La treatments. With an increasing La supply, however, La contents of maize roots were raised less compared to bean roots. La levels in bean roots thus exceeded by far those in maize roots at La concentrations above 5 $\mu\text{mol L}^{-1}$ in nutrient solution. In contrast to bush bean, La supply increased the La content of the maize shoots. Generally, the La contents in roots were markedly higher than those in shoots.

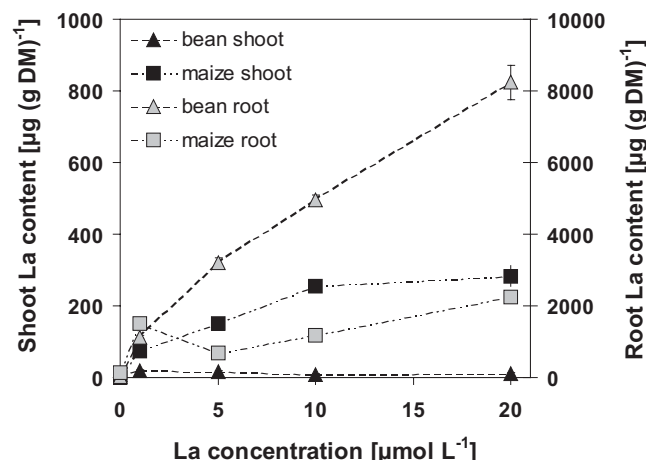


Figure 2: Influence of La concentration in nutrient solution on La contents of roots and shoots of bush bean and maize. Error bars represent standard deviations.

Abbildung 2: Einfluss der La-Konzentration auf den La-Gehalt in Spross und Wurzel von Buschbohne und Mais in Nährlösung. Fehlerbalken geben die Standardabweichung an.

3.2 Plant response to different La concentrations in soil

The growth of bush bean in a sandy soil was not significantly affected by La additions up to 72 $\mu\text{mol La (kg soil)}^{-1}$ (Tab. 2). No yield decrease could be detected. The same was true for spinach. When cultivated in a loamy sand, no decline in biomass production was observed up to a La supplement of 360 $\mu\text{mol (kg soil)}^{-1}$. In contrast, small amounts of La (3.6 $\mu\text{mol (kg soil)}^{-1}$) actually promoted spinach growth by about 20% compared to the control, whereas yield of bush bean was not significantly affected.

The shoots of both bush bean and spinach were analyzed for their La contents. In bean, small amounts of La were found in the shoots of control plants without addition of La. The shoot La content did not differ from the control up to a soil La level

Table 2: Biomass production and shoot La content of bush bean and spinach grown in sandy soils with increasing La contents.**Tabelle 2:** Erträge und La-Gehalte im Spross von Buschbohne und Spinat auf Sandböden mit steigenden La-Gehalten.

Addition of La $\mu\text{mol kg}^{-1}$	Yield		Shoot La content	
	bush bean	spinach	bush bean	spinach
	— g DM plant ⁻¹ —		— $\mu\text{g (g DM)}^{-1}$ —	
0	4.31 a	6.70 a	1.25 a	<0.5 ^(a)
3.6	4.75 a	9.07 b	1.21 a	<0.5
7.2	4.46 a	—	0.89 a	—
14.4	4.50 a	—	1.65 a	—
18.0	—	8.17 a	—	<0.5
36.0	—	8.20 a	—	<0.5
72.0	4.19 a	8.05 a	5.07 b	<0.5
360.0	—	8.15 a	—	<0.5

Different letters within each column indicate statistically significant differences at $p \leq 0.05$.

(a) Detection limit for La in plant material $0.5 \mu\text{g (g DM)}^{-1}$.

of about $14 \mu\text{mol (kg soil)}^{-1}$ (Tab. 2); shoot La contents significantly increased only at the level of $72 \mu\text{mol La (kg soil)}^{-1}$. In spinach, La in the shoots remained below the detection limit at any of the tested soil La levels.

To elucidate the possible reasons for differences in La uptake by the plants, the amount of potentially available La was examined in unplanted treatments by an extraction with 0.1 mol L^{-1} acetic acid (Fig. 3). For low additions, the acetic acid-extractable La did not differ from the levels of native soils without La supplement. Above about $35 \mu\text{mol La (kg soil)}^{-1}$, however, La extractability increased in a dose-dependent fashion in both soils, but only very low amounts of about 0.3% of the added La were extracted. No difference was found between the sandy soil and the loamy sand, in which bush bean and spinach were respectively grown.

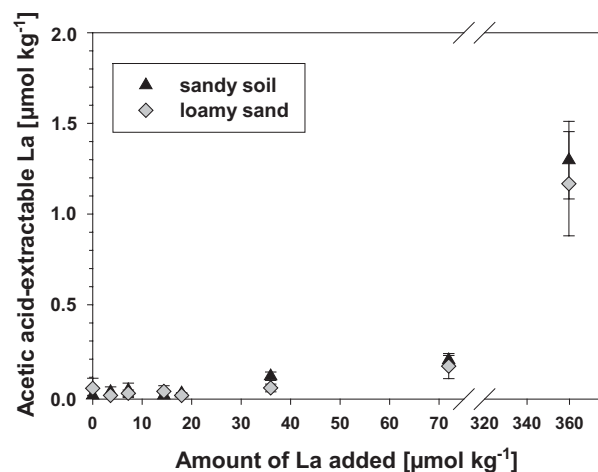
**Figure 3:** Acetic acid-extractable La in two soils supplemented with increasing amounts of La. Error bars represent standard deviations.

Abbildung 3: Essigsäure-extrahierbares Lanthan von zwei mit steigenden La-Mengen beaufschlagten Böden. Fehlerbalken geben die Standardabweichung an.

3.3 Soil factors affecting La extractability

The plant experiments with nutrient solution and soils suggest that the effect of La on the plant depends on both the plant species and the availability of La in the medium. The latter obviously differs between the nutrient solution and soil, but it may also vary between the different soil types. Therefore, to investigate differences in La extractability, La from 12 different soils that were previously spiked with 72 or $720 \mu\text{mol (10 or } 100 \text{ mg La) (kg soil)}^{-1}$ was extracted with 0.1 mol L^{-1} acetic acid. Correlation analyses with selected parameters showed that the amount of acetic acid-extractable La was related mainly to soil pH when moderate amounts of La were added (Tab. 3). In soils with low pH, markedly more La could be extracted. The roles of both CEC and soil organic matter were more pronounced when soils were spiked with high amounts of La. In this case, soils with higher CEC, C_{org} , and pH values adsorbed significantly more La. In addition, higher P concentrations decreased La extractability.

Table 3: Correlation coefficients (r values) between acetic acid-extractable La and various soil parameters.

Tabelle 3: Korrelationskoeffizienten zwischen Essigsäure-extrahierbarem La und Bodeneigenschaften.

	Addition of La to soil [$\mu\text{mol kg}^{-1}$]	
	72	720 (a)
pH	-0.71 ***	-0.76 ***
CEC _{eff} (a)	-0.38 *	-0.84 ***
C_{org} (b)	-0.27	-0.68 ***
P_{CAL}	-0.19	-0.44 **

(a) Data logarithmically transformed

(b) Transformation $1/x$

*** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$

4 Discussion

The investigations presented here demonstrate different effects of La on plant growth. Any of no reaction or an increase or decrease in yield was observed in response to an increased La supply. In nutrient solution, the high sensitivity of the shoot growth of bush bean is in agreement with other reports for mungbean that responded in a decrease of shoot growth at La concentrations higher than $0.2 \mu\text{mol L}^{-1}$ (Diatloff et al., 1995a). Compared to bush bean, maize was highly tolerant to higher La concentrations. The lower sensitivity of maize generally confirms earlier observations (Diatloff et al., 1995a), although no positive effect on root dry weight was noticed in our experiment.

When plants were cultivated in soil, the influence of La was less evident: no toxicity was observed, even for bush bean and at higher La dosages. The buffering capacity for La in soil very likely accounts for this effect (Peverill et al., 1997), and measurements of the soil saturation extracts confirm a high La adsorption in soils, thus resulting in La concentrations of the soil solution far below those tested in nutrient solution. Moreover, in soils La may be detoxified, whether through the formation of nontoxic La complexes with humic and fulvic

acids (Diatloff et al., 1998) or the presence of effective root exudates that are not diluted as in nutrient solution.

The question arises whether these complexes can provide plant-available La. Low-molecular-weight organic acids present in the root rhizosphere (Wang et al., 2001; Han et al., 2005) and the addition of low concentrations of fulvic acids (Gu et al., 2001) and of EDTA (Yang et al., 1999) were found to increase the La bioaccumulation in wheat and barley. Our results indicate that the shoots of bush bean grown in either nutrient solution or in soil are similar and low in La content, showing an increase only in soil at the highest level of $72 \mu\text{mol}$ (10 mg) La (kg soil) $^{-1}$. The resulting La content in the shoots of bush bean was neither harmful nor beneficial for shoot growth. However, it remains unclear and requires further investigation why spinach shoots profited from La additions to soil despite not taking up any detectable amount of La into the shoots. Experiments in nutrient solution with concentrations markedly below $1 \mu\text{mol La L}^{-1}$ may be helpful to clarify the effects of La concentrations comparable to those in La-treated soils.

It has been reported that 0.1 mol L^{-1} acetic acid represents water-soluble, exchangeable, and carbonate-bound La in the soil and therefore is a suitable extractant for describing La bioavailability to plants (Li et al., 1998; Wang et al., 2001; Zhang and Shan, 2001; Shan et al., 2003). However, in the investigation presented here, acetic acid, at least for spinach, was not a good predictor for the La uptake from soil. Pronounced differences between plant species in La uptake most probably account for this. Under natural conditions and in the same site, La contents of different plant species may differ by a factor of 10, not even considering hyperaccumulators like fern species (Ichihashi et al., 1992; Wyttenbach et al., 1998). Moreover, correlations between acetic acid-extractable La and La availability of plants have often only been assessed for root La contents and are sometimes thought to be less valuable for shoots (Zhang and Shan, 2001). When applied to either soil or nutrient solution, La is in a species-dependent manner largely accumulated in the root, thus exceeding by far concentrations of the shoot (Diatloff et al., 1995a; Li et al., 1998; Xu et al., 2002). This agrees fully with our results obtained for the nutrient solution.

Other extractants for the determination of available La have also been proposed: reactants like $\text{Ca}(\text{NO}_3)_2$ (Diatloff et al., 1996), $\text{Mg}(\text{NO}_3)_2$ (Cao et al., 2000), or CaCl_2 , which has been most valuable for spinach (Wang et al., 2004); or even low-molecular-weight organic acids, which simulate conditions in the root rhizosphere (Shan et al., 2003). Any of the extractants might better reflect the La uptake from soil than acetic acid and are worth further investigation, but they are in any case biased by the pronounced differences in La uptake between different species.

Soil extraction with 0.1 mol L^{-1} acetic acid indicated that the La released is closely related to the soil pH value. Several reports (Diatloff et al., 1996; Land et al., 1999; Zhang and Shan, 2001; Shan et al., 2002; Wang et al., 2004) demonstrate that low soil pH is favorable and one of the factors increasing La solubility. Results from the acetic acid extrac-

tion also confirm the relation between La solubility and other factors such as CEC or soil organic-matter content, which was proposed for Chinese soils (Shan et al., 2002; Wang et al., 2004) and the involvement of soil P content in La mobility (Johannesson et al., 1995; Diatloff et al., 1996). Extraction with 0.1 mol L^{-1} acetic acid is thus at least suited to classify soils with respect to their La bioavailability without being able to account for species-related differences of La uptake.

5 Conclusion

Lanthanum may cause damage to sensitive plant species under conditions of high availability. In soil, La solubility and its availability to plants is affected by the application rate of La and soil properties, where soil pH plays a key role. Feed supplementation of La for pigs at the dosages tested to date causes an annual input of about 0.1 mg ($0.72 \mu\text{mol}$) La $\text{kg}^{-1} \text{ y}^{-1}$ to the upper soil layer. This does not seem to be critical for plant growth, even when applied over a longer period of several decades, because an increased La availability to the plant requires specific soil conditions such as low pH and low CEC, organic carbon, or P contents. However, balancing La input via manure and La removal by harvested plants and potential losses by leaching makes clear that La will be accumulated in soils, because plant La uptake is low and La leaching is marginal. Therefore, particularly after long-term application of La, attention should be directed towards factors that may mobilize the accumulated La. To date, no information is available about the reaction of plant species that more strongly acidify the rhizosphere. Also, in assessing the overall effect of La application, the creation of acidifying conditions by changes in land use, such as converting formerly La-treated land to forestry sites, as well as pronounced differences of REE uptake between species have to be taken into account.

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